

# Bishydrazinium and Diammonium Salts of 4,4',5,5'-Tetranitro-2,2'-biimidazolate (TNBI): Synthesis and Properties

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**Abstract:** The diammonium (1) and bishydrazinium (2) salts of 4,4',5,5'-tetranitro-2,2'-biimidazolate (TNBI) were synthesized and their physical properties as well as predicted explosive performance characteristics are described. These dianionic salts are easily formed in good yields by reaction of TNBI with aqueous solutions of the cationic species. TNBI is synthesized from 2,2'-biimidazole, which is ultimately synthesized by the condensation of aqueous glyoxal with ammonium acetate. The compounds were characterized by

NMR spectroscopy, vibrational (FT-IR and Raman) spectroscopy, elemental analysis, thermal analysis (DSC, VTS and calorimetry), and small scale safety testing (impact, friction, ESD). The measured densities and heats of formation are reported. The materials show promise for use in IM explosive and propellant formulations due to the combination of their calculated performances, thermal stability and insensitivity to stimuli.

**Keywords:** Biimidazoles • Explosives • Energetic materials • Nitro compounds • Energetic salts

## 1 Introduction

The synthesis of new powerful yet insensitive energetic compounds is a continuous goal of the energetics community. The isomeric explosive materials 1,4-dinitroimidazole (1,4-DNI) and 2,4-dinitroimidazole (2,4-DNI) have generated much interest due to the low-melting point of the 1,4-isomer (which renders it melt-castable), its tendency with continued heating to undergo thermal rearrangement to 2,4-DNI in the molten state, and the excellent thermal stability/insensitivity to impact of the resulting 2,4-isomer [1]. The related material 4,4',5,5'-tetranitro-2,2'-biimidazole (TNBI) structurally represents two conjoined 2,4-DNI molecules connected by a central C–C bond, resulting in higher density and improved oxygen balance in TNBI when compared to the monocyclic compounds. TNBI has been the subject of much research due to its combination of excellent thermal stability, favorable calculated performance characteristics, and relative insensitivity to stimuli [2]. However, the strong affinity of TNBI towards atmospheric moisture (approximately 10% by weight at 80% relative humidity) has hindered its utility as an energetic ingredient.

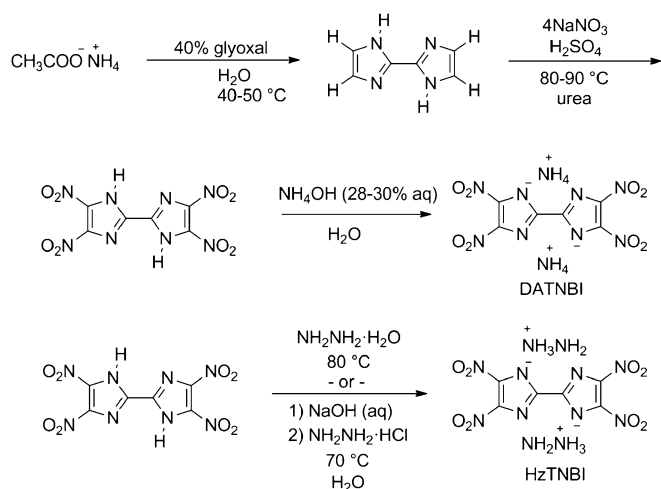
One strategy previously utilized to overcome the inherent hygroscopicity of TNBI is substitution of the hydrogen atoms attached to the imidazole ring hydrogen atoms with covalently bound *N*-amino and *N*-methyl groups. These approaches have been successfully demonstrated on the laboratory scale [3], but with regard to potential scale-up the synthetic processes and the reagents involved [e.g. – mesitylene *O*-sulfonyl hydroxylamine (MSH)] may be problematic. Alternative approaches to solving the hygroscopicity

issues associated with TNBI have focused on the ability of this compound to co-ordinate with metals (for use in pyrotechnic applications) [4] and form the deprotonated energetic di-anion in nitrogen-rich energetic salts. Examples of these latter salts include the 3,6-bishydrazine-1,2,4,5-tetrazinium salt [5] and the more recently described bisguanidinium, bishydroxylammonium, and bis mono-, di- and tri-ami-noguanidinium salts [6].

The crystal structure of the diammonium salt (1) of TNBI has been published [7], but other attributes of the material facilitating accurate estimation of performance characteristics were not measured. This article describes previously unreported properties and explosive performance calculations of the diammonium salt (1) as well as the synthesis, properties and performance calculations for the bishydrazinium salt (2).

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14. ABSTRACT <b>The diammonium (1) and bishydrazinium (2) salts of 4,4â,5,5â,-tetranitro-2,2â,-biimidazolate (TNBI) were synthesized and their physical properties as well as predicted explosive performance characteristics are described. These dianionic salts are easily formed in good yields by reaction of TNBI with aqueous solutions of the cationic species. TNBI is synthesized from 2,2â,-biimidazole, which is ultimately synthesized by the condensation of aqueous glyoxal with ammonium acetate. The compounds were characterized by NMR spectroscopy, vibrational (FT-IR and Raman) spectroscopy, elemental analysis, thermal analysis (DSC, VTS and calorimetry) and small scale safety testing (Impact, Friction, ESD). The measured densities and heats of formation are reported. The materials show promise for use in IM explosive and propellant formulations due to the combination of their calculated performances, thermal stability and insensitivity to stimuli.</b>					
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**Scheme 1.** Synthesis of diammonium (1) and bishydrazinium (2) salts of TNBI.

## 2 Results and Discussion

### 2.1 Synthesis

The synthetic routes utilized are summarized in Scheme 1. The published synthesis of non-energetic precursor 2,2'-biimidazole (BI) from aqueous glyoxal and ammonium acetate [8] was slightly modified to facilitate scale-up with moderate yields of approximately 47–48% BI based on glyoxal. Nitration with sodium nitrate in concentrated sulfuric acid according to literature methods affords TNBI dihydrate in 55–60% yield. [2] The diammonium salt **1** rapidly precipitates from aqueous solutions of TNBI upon addition of aqueous ammonium hydroxide. Similarly, the precipitated dihydrazinium salt **2** is formed by the reaction of an aqueous suspension of TNBI with hydrazine monohydrate. Alternatively, **2** can be synthesized by the formation of the disodium salt of TNBI in water followed by metathesis with

aqueous hydrazine monohydrochloride at elevated temperature, thereby avoiding the handling and use of the flammable and acutely toxic liquid reagent hydrazine monohydrate.

### 2.2 Explosive Performance and Sensitivity Properties

The physical and explosive properties of TNBI salts **1** and **2** are listed in Table 1 along with common nitramine-based explosive RDX and insensitive explosive ingredient NTO for comparison purposes.

Compounds **1** and **2** are extremely thermally stable, as reflected by both the high DSC onset temperatures as well as the extremely low volumes of gas evolved at temperature under vacuum as determined by vacuum thermal stability (VTS) testing. Both TNBI salts rank slightly lower than RDX and NTO with regard to calculated detonation pressure and velocity of detonation, however, the calculated total energies of detonation are significantly higher for the TNBI salts than that of NTO. This suggests that the actual work output of these materials will be significantly better than NTO, in theory approaching that of RDX. The calculated temperatures of detonation for both TNBI salts are also significantly higher than that of NTO. Both salts are quite insensitive to stimuli; the diammonium salt **1** in particular is remarkably insensitive to impact, proving less sensitive than NTO in the BAM Impact tester. This data suggests both salts **1** and **2** may be useful in future IM explosive and propellant applications as potential nitramine replacements.

## 3 Experimental Section

**Caution:** The materials described are energetic/explosive in nature. While they were prepared and handled without incident, they should only be prepared by trained, qualified

**Table 1.** Performance and sensitivity properties.

	RDX	NTO	<b>1</b>	<b>2</b>
Formula	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>10</sub> O <sub>8</sub>	C <sub>6</sub> H <sub>10</sub> N <sub>12</sub> O <sub>8</sub>
FW <sup>a)</sup> [g mol <sup>-1</sup> ]	222.1	130.1	348.2	378.2
T <sub>dec</sub> <sup>b)</sup> [°C]	219	273	269	220
ρ <sup>c)</sup> [g cm <sup>-3</sup> ]	1.816	1.93	1.806 (pyc), 1.805 [7]	1.786 (pyc)
ΔH <sub>f</sub> <sup>d)</sup> [kJ mol <sup>-1</sup> ]	16.7	−129.4	265	184
P <sub>cj</sub> <sup>e)</sup> [GPa]	33.2	33.1	30.9	30.0
D <sub>v</sub> <sup>f)</sup> [km s <sup>-1</sup> ]	8.840	8.767	8.471	8.477
T <sub>det</sub> <sup>g)</sup> [K]	3425.4	2288.1	3266.2	2910.6
OB <sup>h)</sup> [%]	−21.6	−24.6	−36.8	−38.1
IS <sup>i)</sup> [cm]	29.8 (7.3 J)	82.5 (20.2 J)	> 100 (> 24.5 J)	49.2 (12.1 J)
FS <sup>j)</sup> [N]	168	> 360	> 360	360
ESD <sup>k)</sup> [J]	–	–	> 0.25	> 0.25J
Tot E of Det <sup>l)</sup> [kJ cm <sup>-3</sup> ]	10.4	7.26	9.37	9.04
VTS <sup>m)</sup> [mL g <sup>-1</sup> ] at 100 °C per 48 h	–	0.20	0.010	0.044

a) FW = formula weight. b) T<sub>dec</sub> = temperature of decomposition. c) ρ = density. d) ΔH<sub>f</sub> = heat of formation. e) P<sub>cj</sub> = CJ Pressure. f) D<sub>v</sub> = velocity of detonation. g) T<sub>det</sub> = temperature of detonation. h) OB = oxygen balance. i) IS = impact sensitivity in cm (converted to PE [J]). j) FS = friction sensitivity. k) ESD = electrostatic discharge. l) Tot E of Det = total energy of detonation. m) VTS = vacuum thermal stability.

and authorized individuals working in a suitable environment using proper safety precautions and protocols.

### 3.1 General Considerations

All starting materials were purchased from Aldrich Chemical and used without further purification unless otherwise indicated. Differential scanning calorimetry (DSC) measurements were recorded with a Perkin-Elmer DSC 4000 with a scan-rate of 5 °C per minute.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance 400 MHz NMR spectrometer. Infrared spectra were recorded with a Perkin-Elmer Frontier FT-IR with Diamond ATR. Raman spectra were obtained with a confocal Horiba-Jobin Yvon LabRam micro-Raman spectrometer with a 20 mW HeNe laser source emitting at a wavelength of 632.8 nm focused to a spot size of 10  $\mu\text{m}$  with a 10 $\times$  lens. The system was run at maximum laser intensity, with the following parameters: 300  $\mu\text{m}$  hole, 200  $\mu\text{m}$  slit, 2 $\times$ 15 sec acquisition time. Calorimetry samples were run with a Parr Instruments Calorimetric Thermometer and Semimicro Calorimeter (30 atm, (3.4 MPa) oxygen with 2  $\text{cm}^3$  of de-ionized water in the cell). For each experiment the sample (ca. 0.15 g) was hand-pressed into a pellet. Proper function and measurement was validated with a benzoic acid standard just prior to testing. Complete combustion was evident by absence of residue on bomb walls. The water in the bomb was rinsed and titrated for nitric acid formation in the combustion products. Impact sensitivity tests were carried out according to STANAG 4489 [9] using an ERL impact tester with a 2.5 kg weight. Friction sensitivity tests were carried out according to STANAG 4487 [10] using the BAM friction tester. Electrostatic discharge sensitivity tests were carried out using an electric spark tester (Albany Ballistic Laboratories). VTS testing was conducted according to STANAG 4556 [11] measuring the volume of gas evolved under vacuum at 100 °C for 48 h. Explosive performance values for CJ Pressure, detonation velocity, temperature of detonation, and total energy of detonation were all calculated with CHEETAH 6.0 using the exp 6.3 library. The performance values as reported for NTO and RDX are provided for comparison purposes and were generated using the CHEETAH 6.0 reactant library values for heat of formation and density for these materials.

### 3.2 Synthetic Procedures

#### 3.2.1 Synthesis of 2,2'-Biimidazole (BI)

Ammonium acetate (1593 g, 20.67 mol) was slurried in de-ionized water (1000 mL) and heated to 40 °C with heating mantle with stirring. The heating source was turned off and glyoxal (1122 g of 40% aqueous glyoxal; 7.73 mol) was added dropwise with stirring over the course of 5 h such that the heat of reaction maintained the reaction temperature at 40–50 °C throughout the addition. The reaction was

cooled to room temperature and the resulting precipitated product was collected by vacuum filtration and dried in an air-swept oven at 60 °C overnight yielding 163.2 g (1.22 mol) of solid BI (47.2% based on glyoxal), which matches previously reported properties for this material [8].

#### 3.2.2 Diammonium-4,4',5,5'-tetranitro-2,2'-biimidazolate (1)

4,4',5,5'-Tetranitro-2,2'-biimidazole dihydrate (10.00 g, 28.56 mmol) was suspended in 250 mL of deionized water. Ammonium hydroxide 28–30%  $\text{NH}_3$  (10.0 mL, 71.9 mmol, 2.5 equiv.) was added dropwise while stirring. The resulting pale yellow suspension was stirred at 20 °C for 24 h and then cooled to 5 °C. The yellow solid product was collected by vacuum filtration, washed with 50 mL of isopropyl alcohol, air-dried for 1 h, and further dried in a vacuum oven at 60 °C for 24 h yielding 9.45 g (27.14 mmol) of **1** as yellow needles (95%). **DSC** (5 °C  $\text{min}^{-1}$ ):  $T_{\text{dec}} = 269^\circ\text{C}$ ; **EA** for  $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_8$  (348.2  $\text{g mol}^{-1}$ ): C 20.70 (calcd. 20.93), N 40.23 (39.16), H 2.32 (2.22)%.  **$^1\text{H}$  NMR** ( $\text{DMSO}-d_6$ , 25 °C, ppm):  $\delta = 3.58$  (br. s, 3 H).  **$^{13}\text{C}$  NMR** ( $\text{DMSO}-d_6$ , 25 °C, ppm):  $\delta = 140.19$ , 143.84. **IR** (ATR):  $1/\lambda = 3210$  (m, br), 2927 (w), 2721 (m, br), 2486 (w), 1475 (s), 1441 (s), 1387 (s), 1365 (s), 1304 (s), 1242 (s), 1114 (s), 950 (m), 854 (s), 810 (s), 754 (s), 706 (m)  $\text{cm}^{-1}$ . **Raman**:  $1/\lambda$  (%) = 1561 (100), 1553 (20), 1484 (5), 1476 (28), 1386 (15), 1342 (30), 1300 (76), 1255 (93), 1024 (30), 864 (33), 809 (9), 768 (19), 755 (19), 686 (8), 660 (8), 524 (7), 427 (8), 391 (10)  $\text{cm}^{-1}$ . **Sensitivities**: IS >100 cm (>24.5 J), FS: 10 No Go at 360 N; ESD: 20 No Go at 0.25 J. **Density** (helium pycnometry): 1.8065  $\text{g cm}^{-3}$ .  $\Delta H_{\text{f}}(\text{measured})$ : +265  $\text{kJ mol}^{-1}$ . VTS (0.04  $\text{mL g}^{-1}$  at 100 °C per 48 h).

#### 3.2.3 Bishydrazinium-4,4',5,5'-tetranitro-2,2'-biimidazolate (2) via Deprotonation with Hydrazine Monohydrate

4,4',5,5'-Tetranitro-2,2'-biimidazole dihydrate (3.50 g, 10.0 mmol) was suspended in de-ionized water (50 mL) and heated to 80 °C. Hydrazine monohydrate (1.10 mL, 1.10 g, 22.0 mmol) was added dropwise with stirring at temperature. The resulting bright orange suspension was stirred at temperature for 30 min and then cooled to room temperature. The resultant orange solid precipitate was collected by vacuum filtration, washed with cold water (300 mL), air dried for 1 h and further dried in a dessicator under vacuum to constant weight of 3.545 g (9.37 mmol) of **2** as orange needles (94%).

#### 3.2.4 Bishydrazinium-4,4',5,5'-tetranitro-2,2'-biimidazolate (2) via Metathesis with Hydrazine Monohydrochloride

4,4',5,5'-Tetranitro-2,2'-biimidazole dihydrate (40.00 g, 114.2 mmol) was suspended in de-ionized water (700 mL). A solution of sodium hydroxide (9.12 g, 228.5 mmol) in water (100 mL) was added dropwise with stirring. The resulting bright orange suspension was heated with stirring (became orange solution at approximately 58 °C). When the

reaction temperature reached 65 °C a solution of hydrazine monohydrochloride (15.75 g, 229.9 mmol) in water (50 mL) was added dropwise over the course of 10 min with vigorous stirring; a flocculent orange precipitate immediately formed with each drop. The reaction was further heated and stirred at 70–75 °C for 1 h, after which it was allowed to cool to room temperature. The resultant orange solid precipitate was collected by vacuum filtration, washed with cold water (200 mL), air dried for 1 h and further dried in a vacuum oven at 60 °C for 24 h yielding 40.941 g (108.2 mmol) of **2** as orange needles (95%). **DSC** (5 °C min<sup>-1</sup>):  $T_{\text{dec}} = 220$  °C; **EA** for C<sub>8</sub>H<sub>10</sub>N<sub>12</sub>O<sub>8</sub> (378.2 g·mol<sup>-1</sup>): C 19.05 (calcd. 19.37), N 44.44 (43.35), H 2.63 (2.66)%. **<sup>1</sup>H NMR** (DMSO-*d*<sub>6</sub>, 25 °C, ppm):  $\delta = 7.32$  (br. s, 6 H). **<sup>13</sup>C NMR** (DMSO-*d*<sub>6</sub>, 25 °C, ppm):  $\delta = 140.19, 143.86$ . **IR** (ATR):  $1/\lambda = 3353$  (m), 3341 (m), 3235 (m, br), 2602 (m, br), 1626 (w), 1595 (w), 1541 (m), 1515 (m), 1469 (s), 1394 (s), 1368 (s), 1308 (s), 1268 (m), 1115 (s), 1104 (m), 1088 (s), 973 (s), 953 (m), 854 (s), 810 (s), 753 (m), 704 (m), 663 (w) cm<sup>-1</sup>. **Raman**:  $1/\lambda$  (%) = 1559 (81), 1539 (36), 1503 (19), 1474 (52), 1387 (27), 1303 (78), 1249 (100), 1108 (18), 1029 (36), 973 (12), 865 (42), 809 (18), 769 (16), 752 (16), 697 (12), 682 (11), 652 (11), 651 (11), 524 (10), 440 (11), 426 (12), 392 (15) cm<sup>-1</sup>. **Sensitivities**: IS 49.2 cm (12.1 J), FS: 10 No Go at 360 N; ESD: 20 No Go at 0.025 J. **Density** (helium pycnometry): 1.79 g cm<sup>-3</sup>.  $\Delta H_{\text{f(measured)}}$ : +184 kJ mol<sup>-1</sup>. VTS (0.044 mL g<sup>-1</sup> at 100 °C per 48 h).

## 4 Conclusions

The diammonium (**1**) and bis(hydrazinium) (**2**) salts of TNBI can be synthesized in good yields from inexpensive and widely available starting materials. The salts are both extremely insensitive to stimuli such as impact, friction, and electrostatic discharge (ESD). The calculated performance characteristics of these materials based on their measured densities and measured heats of formation compare favorably with common nitramine RDX, particularly with regard to total energy of detonation. This suggests that these materials may find utility in future IM explosive and propellant applications as nitramine replacements.

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## References

- [1] a) R. Damavarapu, K. Jayasuriya, T. Vladimiroff, S. Iyer, *2,4-Dinitroimidazole—A Less Sensitive Explosive and Propellant Made By Thermal Rearrangement of Molten 1,4-Dinitroimidazole*, US Patent 5,387,297, The United States Of America As Represented By The Secretary Of The Army, Washington, DC, USA, **1992**; b) K. Jayasuriya, R. Damavarapu, R. L. Simpson, C. L. Coon, M. Coburn, *2,4-Dinitroimidazole: A Practical Insensitive High Explosive?* LLNL, UCRL-ID-1133G4, Livermore, CA, USA, **1993**; c) R. Simpson, C. Coon, M. Foltz, *A New Insensitive Explosive That Has Moderate Performance and is Low Cost: 2,4-Dinitroimidazole* LLNL, UCRL-ID-119675, Livermore, CA, USA, **1995**.
- [2] a) D. T. Cromer, C. B. Storm, *Structure of 4,4',5,5'-Tetranitro-2,2'-Bi-1H-imidazole Dihydrate*, *Acta Crystallogr. Sect. C* **1990**, *46*, 1957; b) S. G. Cho, J. R. Cho, E. M. Goh, J.-K. Kim, *Synthesis and Characterization of 4,4',5,5'-Tetranitro-2,2'-Bi-1H-imidazole (TNBI)*, *Propellants Explos. Pyrotech.* **2005**, *30*, 445; c) C. Li, Y. Jian, L. Liu, Z. Li, S. Zhang, *Synthesis Method of 4,4',5,5'-Tetranitro-2,2'-biimidazole*, Faming Zhuanli Shenqing CN Patent 102304089A, China Petroleum & Chemical Corporation, Beijing, P. R. China, **2011**.
- [3] M. M. Breiner, D. E. Chavez, D. A. Parrish, *Nucleophilic Reactions of The Bis Ammonium Salt of 4,4',5,5'-Tetranitro-2,2'-biimidazole*, *Synlett* **2013**, *24*, 519–521.
- [4] T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Energetic Derivatives of 4,4',5,5'-Tetranitro-2,2'-bisimidazole (TNBI)*, *Z. Anorg. Allg. Chem.* **2012**, 1278–1286.
- [5] D. E. Chavez, M. A. Hiskey, *1,2,4,5-Tetrazine Based Energetic Materials*, *J. Energ. Mater.* **1999**, *17*, 357.
- [6] a) T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Energetic Derivatives of 4,4',5,5'-Tetranitro-2,2'-bisimidazole (TNBI)*, *Z. Anorg. Allg. Chem.* **2012**, 1278–1286; b) D. E. Chavez, D. Parrish, D. N. Preston, I. W. Mares, *Synthesis and Energetic Properties of 4,4',5,5'-Tetranitro-2,2'-biimidazolate (N4BIM) Salts*, *Propellants Explos. Pyrotech.* **2012**, 647–652.
- [7] a) D. T. Cromer, C. B. Storm, *Structure of the Diammonium Salt of 4,4',5,5'-Tetranitro-2,2'-biimidazole*, C<sub>8</sub>H<sub>10</sub>N<sub>12</sub>O<sub>8</sub>·2NH<sub>4</sub>, *Acta Crystallogr., Sect. C* **1990**, *46*, 1959; b) S. H. Kim, J. S. Kim, *High Nitrogen Energetic Salts of 4,4',5,5'-Tetranitro-2,2'-Biimidazole*, *Bull. Korean Chem. Soc.* **2013**, *34*, 2503.
- [8] a) J. R. Cho, S. G. Cho, E. M. Goh, J. K. Kim, *Preparation Method of 2,2'-Bi-1H-imidazole Using Glyoxal and an Ammonium Salt*, US 6713631 B2, FR Patent 2,838,440, Agency For Defense Development, Seoul, Republic of Korea, **2002**; b) J.-C. Xiao, J. M. Shreeve, *Synthesis of 2,2'-Biimidazolium-Based Ionic Liquids: Use as a New Reaction Medium and Ligand for Palladium-Catalyzed Suzuki Cross-Coupling Reactions*, *J. Org. Chem.* **2005**, *70*, 3072–3078.
- [9] *NATO Standardization Agreement (STANAG) on Explosives: Impact Sensitivity Tests*, no. 4489, 1st ed., September 17, **1999**.
- [10] *NATO Standardization Agreement (STANAG) on Explosive: Friction Sensitivity Tests*, no. 4487, 1st ed., August 22, **2002**.
- [11] *NATO Standardization Agreement (STANAG) on Explosives: Vacuum Stability Test*, no. 4556, 1st ed., November 22, **1999**.

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